HEAVY METALS DISTRIBUTION IN WATER AT PERAI RIVER

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By

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I hereby declare that all corrections and comments made by the supervisor(s)and examiner have been taken into consideration and rectified accordingly.

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ABSTRAK

Sungai Perai adalah sungai terpanjang di Pulau Pinang dan kawasan tadahan air terbesarnya. Ia telah dikenal pasti sebagai sumber air masa depan yang berpotensi untuk memenuhi permintaan air yang semakin meningkat di negeri ini. Walau bagaimanapun, kualiti air sungai menjadi perhatian utama kepada pengambilan air, yang seterusnya boleh menjejaskan kos rawatan. Ini disebabkan oleh peningkatan pembuangan sisa industri dan domestik yang tidak dirawat terus ke dalam sungai. Akibatnya, air sungai berpotensi dicemari oleh logam berat, yang berbahaya kepada kesihatan awam. Oleh itu, objektif utama kajian ini adalah untuk menilai taburan spatial dan temporal logam berat di dalam air di Sungai Perai. Selain itu, kajian ini bertujuan untuk menganalisis korelasi antara logam berat dengan dua parameter indeks kualiti air (WQI) yang penting iaitu permintaan oksigen biokimia (BOD) dan permintaan oksigen kimia (COD). Bagi menjalankan penyelidikan, sampel air telah diambil daripada 31 titik persampelan, yang merangkumi 11 mata di sungai utama (MR 1-11) dan 20 mata di anak sungai (TR 1-20). Proses persampelan dijalankan sebanyak tiga kali, iaitu dua kali pada musim lembap pada Disember 2021 dan Februari 2022, dan sekali pada musim kemarau pada April 2022. Ujian makmal seperti Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), BOD5 dan Ujian COD telah dijalankan menggunakan sampel air yang dikumpul. Daripada ujian ICP-OES, logam berat ketara yang terdapat dalam air sungai dikenal pasti sebagai merkuri (Hg), aluminium (Al), besi (Fe) dan mangan (Mn). Punca utama pencemaran logam berat di kawasan kajian dikenal pasti adalah pembuangan sisa industri dan domestik secara terus ke dalam sungai. Sebagai bukti konkrit, kepekatan merkuri di sungai Perai dilihat berada dalam julat membimbangkan iaitu 0.97 – 5.66 ppm di kawasan Mak Mandin yang merupakan sebuah bandar perindustrian terkemuka di

Butterworth, Pulau Pinang. Selain itu, sisa domestik daripada TR 12, TR 13 dan TR 14 mengalir terus ke MR 7 menyebabkan taburan terkumpul besi yang tinggi pada MR 7 (6 ppm). Dari segi taburan temporal, kepekatan logam berat dijangka lebih rendah pada musim hujan berbanding musim kemarau disebabkan oleh pencairan semasa hujan lebat. Sebagai contoh, kepekatan aluminium terendah dalam air sungai Perai direkodkan pada 0 ppm di MR 8 semasa musim hujan Februari 2022. Namun, dalam beberapa kes, keputusan kepekatan logam berat yang diperolehi membuktikan sebaliknya mungkin disebabkan oleh kesengajaan. pembuangan sisa industry dalam kuantiti yang besar semasa musim hujan untuk mengurangkan keterlihatan. Sebagai bukti yang kukuh, kepekatan mangan didapati paling tinggi (0.64 ppm) pada April 2022 (musim kemarau) dan terendah (0.06 ppm) pada Februari 2022 (musim hujan). Korelasi antara logam berat, BOD dan COD dianalisis menggunakan analisis bivariat SPSS. Kolerasi yang sangat ketara dilihat antara Fe – COD, manakala korelasi yang sedikit ketara dilihat antara; Hg–COD, dan Fe–BOD. Graf regresi kepekatan COD terhadap kepekatan Hg telah diplot kerana ia adalah satu-satunya pasangan parametrik dengan korelasi yang signifikan. Garisan penyuaian terbaik telah dilukis, mentafsirkan bahawa COD meningkat secara linear dengan Hg.

ABSTRACT

Perai River is Penang’s longest river and its largest water catchment area. It has been identified as a potential future water source to serve the state’s growing water demands. However, the quality of the river water is a major concern to water intake, which subsequently can also affect the treatment cost. This is due to the increased discharge of untreated industrial and domestic wastes directly into the river. Consequently, the river water could potentially be polluted by heavy metals, which are harmful to public health. Therefore, the main objective of this study is to assess the spatial and temporal distribution of heavy metals in the water at Perai River. In addition, the study aims to analyse the correlation between heavy metals and two important water quality index (WQI) parameters which are biochemical oxygen demand (BOD) and chemical oxygen demand (COD). In order to conduct the research, water samples were collected from 31 sampling points, which include 11 points in the main river (MR 1-11) and 20 points in the tributaries (TR 1-20). The sampling process was carried out thrice, whereby twice during the wet seasons of December 2021 and February 2022, and once during the dry season of April 2022. Laboratory tests such as Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), BOD_5 and COD tests were conducted using the water samples collected. From the ICP-OES test, the significant heavy metals present in the river water were identified to be mercury (Hg), aluminium (Al), iron (Fe) and manganese (Mn). The main sources of heavy metal pollution in the study area were identified to be the direct industrial and domestic waste discharge into the river. As concrete evidence, mercury concentration in Perai river was noticed to be in the alarming range of 0.97 – 5.66 ppm in Mak Mandin area which is a prominent industrial town in Butterworth, Penang. Besides that, the residential waste from TR 12, TR 13 and TR 14

flow directly to MR 7 causing the high cumulative distribution of iron at MR 7 (6 ppm). In terms of temporal distribution, the concentration of heavy metals was expected to be lower in the wet seasons compared to the dry seasons due to dilution during heavy rainfalls. For instance, the lowest aluminium concentration in Perai river water was recorded to be at 0 ppm in MR 8 during the wet season of February 2022. However, in some cases, the results of the heavy metals concentration obtained proved otherwise possibly due to the intentional discharge of a large amount of accumulated industrial waste during the wet seasons to reduce noticeability. As substantial proof, manganese concentration was found to be the highest (0.64 ppm) in April 2022 (dry season) and the lowest (0.06 ppm) in February 2022 (wet season). The correlations between heavy metals, BOD and COD were analysed using SPSS bivariate analyses. A very significant correlation was seen between Fe – COD, whereas a slightly significant correlation was seen between; Hg–COD, and Fe–BOD. A regression graph of COD concentration against Hg concentration was plotted since it was the only parametric pair with correlation significance. A best-fit line was drawn, interpreting that COD increases linearly with Hg.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Background Study

Water plays an important role in regional economic development as well as being a water source for industrial, domestic, agricultural, aquaculture, hydroelectric power generation and the environment (Mei *et al.*, 2017). The consumptive water demand is expected to increase from 14.8 BCM to 18.2 BCM from the year 2010 until the year 2050 respectively (National Water Resources Study, 2011).

In Malaysia, rivers contribute to more than 90% of raw water supply in the domestic sector, agriculture, industry and other developments. However, due to the frequent overlap of two or more states' river basins in Malaysia, water disputes are frequent. Federal-state conflicts complicate and exacerbate water disputes between states (Kedah and Penang for this case) over the use of the Muda River. These conflicts are exacerbated by worries about population growth, urbanisation, the economy, and politics (Mei *et al.*, 2017). Water conflicts between Kedah and Penang started in 2002 when Kedah State Government proposed helicopter logging in the Ulu Muda forests (Azhar, 2000). The 4210 km2 water catchment area that provides up to 96 percent of Kedah's and 80 percent of Penang's water supplies will be destroyed and degraded by the logging of the Ulu Muda forests, which will have an impact on the livelihoods of more than two million people in both states (Mei *et al.*, 2017).

According to the “Master Plan Study for Potable Water Supply in Penang until 2050”, Muda River may only be Penang's sole reliable source of primary raw water until 2025. Without access to a second significant raw water resource, Penang faces a significant risk of a water supply catastrophe by 2025 (Jaseni, 2020). Alternative water technologies are among the measures being looked at when reviewing the Penang Water Supply Initiative 2050 (PWSI 2050) projects (Chow, 2021). Penang Water Supply Corporation (PBAPP), a state-owned company that manages water supply in Penang has outlined three contingency plans under its Penang Water Supply Initiative 2050 (PWSI 2050) to ensure the security of the state's raw water supply (Dermawan, 2020b). One of the contingency plans is the Sungai Perai Water Supply Scheme (SPWSS) which is aimed at using the Perai River as an additional raw water resource with a potential yield of 136 million litres per day (Mok, 2020).

1.2 Problem Statement

Perai River is Penang's longest river and is also its largest water catchment area. It has been identified as a potential future water source to serve the state's growing water demands and catalyst for Butterworth's urban regeneration. However, the pressures of growth and urbanisation have degraded the waters of Perai River to an undesirable level.

The quality of the river water is a major concern to water intake which subsequently can also affect the treatment cost. This is due to the high number of industrial and residential activities along the shores of Perai River which led to the increased discharge of untreated industrial and domestic wastes directly into the river. Consequently, the river water could potentially be polluted by heavy metals which are harmful to public health.

Heavy metals are non-destructive, non-biodegradable, and the most persistent pollutants in the aquatic system. Continuous accumulation of heavy metals in the river water column, sediment, and aquatic organisms is the driving cause of river impairment. For instance, thousands of dead fishes were found floating in Perai River during high tide due to untreated detergents released by a food industry on the 9th of February 2021 (Dermawan, 2021). Detergents contain many organic compounds and heavy metals such

Iron (Fe) and Manganese (Mn). This incident further solidifies the importance of testing Perai River water for the presence of heavy metals beforehand to ensure if it is safe to be used as a raw water source for Penang.

1.3 Objectives

This research aims to evaluate the heavy metal pollution in the water of Perai River. Based on the assessment, the suitability of tapping Perai River water to be used as an alternative raw water source for Penang can be identified. Thus, the objectives of this study are:

- To assess the temporal and spatial distribution of heavy metals in water at Perai River.
- To identify the relationship between heavy metal distribution and biochemical oxygen demand (BOD).
- To determine the relationship between heavy metal distribution and chemical oxygen demand (COD).

1.4 Scope of Study

This study focuses on the downstream of Perai River. Perai River is a major river in Seberang Perai, Penang which separates Butterworth to the north from Perai to the south. As it approaches the river mouth, the river widens substantially. Being the main river in this area, Perai River has numerous tributaries in areas such as Mak Mandin, Bagan, Perai and Seberang Jaya.

In order to prevent a water crisis in Penang in the near future, Penang Water Supply Corporation (PBAPP) implemented Sungai Perai Water Supply Scheme

(SPWSS) which aims to use Perai River as an additional raw water resource. However, the river may be polluted with harmful heavy metals due to anthropogenic activities which can deteriorate public health. Hence, the scope of this study is to identify the types of heavy metals present and their temporal and spatial distribution along the downstream of Perai River by conducting ICP-OES test using the water samples collected. The spatial distribution will be determined using GIS mapping (ArcGIS) which will also help in identifying the potential sources of heavy metals. Besides that, the research would also cover the study of the relationship between heavy metal distribution and two important water quality index (WQI) parameters which are Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD).

1.5 Significance of Study

Heavy metals can be transported or spread in the form of aqueous. This study is significant when it comes to identifying the pollution level in Perai River and producing a clear distribution pattern of the heavy metals present in the water. Hence, the potential sources of heavy metals can be identified and appropriate actions can be taken to reduce the pollution. The findings will also help to identify the correlation between heavy metals and both biochemical oxygen demand (BOD) and chemical oxygen demand (COD) in water. With these assessments, proper decision-making can be done on the suitability of water tapping at Perai River in order to be used as an alternative raw water source for Penang.

1.6 Dissertation Outline

This thesis paper consists of five chapters namely Introduction, Literature Review, Methodology, Results and Discussions, and Conclusion and Recommendations.

Chapter 1:

This chapter includes a brief introduction to the study, the problem statement, the objective of the study, the expected outcome and the importance of the study. This chapter will help give brief information and an overview of the content of the dissertation.

Chapter 2:

This chapter includes past journals/research papers that correlate to the project title and objectives of the project. This chapter sets out the theoretical context for the thesis and outlines the topic, the ongoing state water crisis and actions taken by the state government to overcome the issue, the pollution level of river water and the effects of harmful heavy metal presence in the water. This chapter also provides an in-depth understanding of biochemical oxygen demand (BOD) and chemical oxygen demand (COD) and the impacts of their presence in excess in river water.

Chapter 3:

This chapter contains the method of study of the dissertation. In further depth, the study technique and research methodology (from sampling processes until obtaining valid results) are also discussed.

Chapter 4:

This chapter includes a detailed discussion of data analyses obtained from laboratory works. The data analysed would include the spatial and temporal distribution of heavy metals, and the correlation between heavy metals, biochemical oxygen demand (BOD) and chemical oxygen demand (COD).

Chapter 5:

This chapter concludes the findings of this study and some recommendations were provided for the improvement of future studies.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview of Chapter

Several topics will be reviewed within this chapter, such as the water supply crisis in Penang and the inter-state dispute with Kedah over the use of Muda River. Besides that, this chapter focuses on the suitability, benefits and drawbacks of tapping Perai River water as an alternative raw water resource. In addition, the current river water pollution level in Malaysia, point and non-point sources of pollution and factors affecting river pollution are also reviewed in this chapter. Moreover, this chapter focuses on heavy metals, biochemical oxygen demand (BOD), chemical oxygen demand (COD) and their impacts on the environment and public health when present in excess in river water.

2.2 Water Supply Crisis in Penang

Water is abundant in Malaysia, with an average annual rainfall of 3000 mm, equivalent to about 990 billion m^3 (Farhana and Rais, 2012). However, in recent years, Malaysia has been experiencing water scarcity in certain states due to inadequate water resources recharge, high water demand, pollution, degradation of catchments, low-efficiency water in agriculture, institutional and legal issues (Ti and Facon, 2002). Other factors leading to water scarcity in Malaysia include the growth in population, rapid expansion in urbanisation and industrialisation. Plans of developing new additional water resources require a high budget, besides having to face stringent criticism from environmentalists and conservationists. The escalating water demand despite the limited availability of usable water, proves the unsustainability of supply approach in water management (Abidin, 2004).

The state of Penang is no exception among some of the Malaysian states that are facing a water crisis. The effective capacity of Air Itam dam (which acts as one of Penang's main dams) dropped to an 'Alert Level' of only 38.5% (shown in Table 2.1) due to very high demand for water. The state's water consumption was measured to be at a staggering amount of almost 900 million litres per day (MLD) (Jaseni, 2022).

In Malaysia, the State Governments are accountable for natural resources such as developments, operation and maintenance of water supplies, land and forest (Ti and Facon, 2002; Azhar, 2000). Water supply matters fall under the jurisdiction of the Federal Government only when there is an inter-state water dispute arising from river basins or water reservoirs crossing state boundaries (Azhar, 2000).

Table 2. 1: Effective Capacities of Major Dams in Penang
(Source: PBAPP, 2022; https://pba.com.my/pdf/news/2022/02042022_PBAPP_Dry-Season-Water-Supply-Alert-1-2022.pdf)

Dam		Effective capacity 1.1.2022	Effective capacity 31.3.2022
1.	**Air Itam Dam**	**89.3%**	**38.5%**
2.	Teluk Bahang Dam	87.8%	73.5%
3.	Mengkuang Dam	93.2%	91.4%

2.2.1 Water Dispute over Muda River

Muda River basin crosses the state boundary of two northern states in Peninsular Malaysia, namely Kedah and Penang. This situation inevitably leads to water disputes over the use of the Muda River. The upstream and middle streams belong to Kedah, while the downstream section forms an interstate boundary between Kedah and Penang (Figure 2.1). The length of Muda River is 180km and has a drainage area of 4,210 km^2. Muda River basin covers 329,760 km^2 of total land surface area in Malaysia, of which 160,000 hectares are forest, namely Ulu Muda Forest (Mei *et al.*, 2017). Ulu Muda forest is the headwater of the basin and serves as an essential water catchment for both states. However, the logging of the Ulu Muda Forest reserve by the Kedah State Government sparked inter-state water disputes between Penang and Kedah. Water resources for more than two million people in Kedah and Penang are threatened by logging at Muda River's headwaters (Mei *et al.*, 2017).

According to the 'Masterplan Study for Potable Water Supply in Penang until the Year 2050' commissioned by PBAPP in 2009, Muda River may reliably serve as Penang's only primary raw water resource only until 2025 (Jaseni, 2019). Besides that, the major El Nino event in 2016 drastically depleted the Muda Dam's water storage capacities to critical levels of 45.2% (Tan *et al.*, 2019). Hence, the water supply from Muda River cannot be depended upon for long. In order to avoid a water supply crisis, Penang should tap a second major raw water resource as soon as possible.

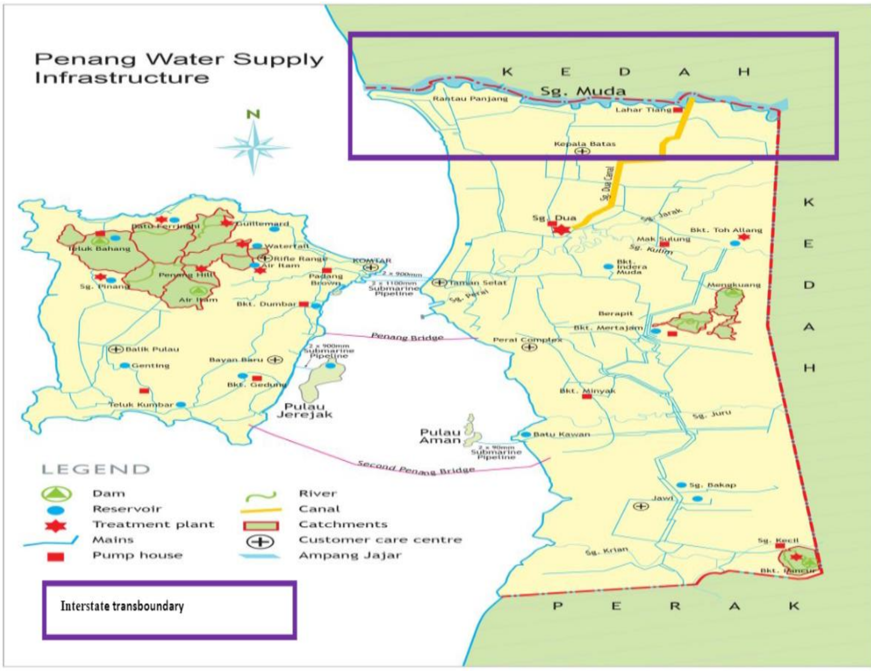

Figure 2.1: Muda River forming an Inter-State Boundary between Kedah and Penang (Source: PBAPP, 2015; http://pba.com.my/?page_id=571)

2.2.2 Perai River as Raw Water Source

Penang's water consumption is anticipated to increase to 1,483 MLD by 2030, 1,696 MLD by 2040, and 1,884 MLD by 2050 (Dermawan, 2019). The initial PWSI 2050 contingency projects proposed in 2019 include Sungai Perai Water Supply Scheme (SPWSS). The potential yield from tapping Perai River water was projected to be 136 million litres per day (PBA, 2020). Perai River falls entirely under the state of Penang, which automatically eliminates any possibility of inter-state disputes over water use. With the tapping of Perai River water, the state of Penang would no longer have to depend on buying raw water supplies from neighbouring states such as Kedah (Muda River) and Perak (Perak River). As a result, Penang state would undeniably witness a boon in the state's economy. However, the raw water from this river may not be safely processed using traditional water treatment techniques, according to earlier water engineering research. Thus, in order to safely treat raw water for human consumption, the SPWSS will investigate the feasibility of using alternative water treatment methods (Dermawan, 2020a). This indicates the significance of conducting further research on the harmful pollutants which deteriorate the river water quality before the commencement of the water treating process.

2.3 River Water Pollution

Water contamination is a serious issue in Malaysia that threatens the long-term reliability of water resources. Additionally, it affects the health of people and the economy of the nation as well as living plants and critters. While some pollution comes from natural sources, human activity is the main cause of most pollution sources. Data show a yearly downward trend, which raises concerns about water contamination (Afroz and Rahman, 2017). Unfortunately, the large quantity of water resources available in the catchment does not guarantee adequate supply to all users because of the river pollution (Ling and Bao, 2010).

Within our river catchments, urbanisation has caused an increase in population and urban life activities. The quality of run-off within a catchment is usually altered due to urbanisation, which impacts the water quality of receiving waters. Rainfall washes toxins deposited on land surfaces into stormwater systems in developed areas. Wastewater from residential, commercial, and industrial locations has a terrible odour, especially when rubbish is present, degrades stormwater quality, and pollutes the existing river system. Most pollution sources are caused by human activities, while some pollution comes from natural sources. Water contamination is becoming a more serious concern, with data indicating a declining trend yearly (Afroz and Rahman, 2017). Water pollution is not a new environmental problem as it has long been associated with urbanisation and modernity.

If the river water is not contaminated by human activity, it is generally potable (suitable for human consumption) with minimal treatment (Ghale, 2022). However, rivers are now used to dispose of liquid and solid wastes. The water quality trend in Malaysian river basins from 2005 to 2011 is depicted in Figure 2.2. While the government is mainly responsible for addressing river pollution issues, a fundamental aspect such as water supply necessitates the education and participation of end-users. When a body of water is harmed by the addition of little or large volumes of materials (pollutants), it is called water pollution (Afroz *et al.*, 2014).

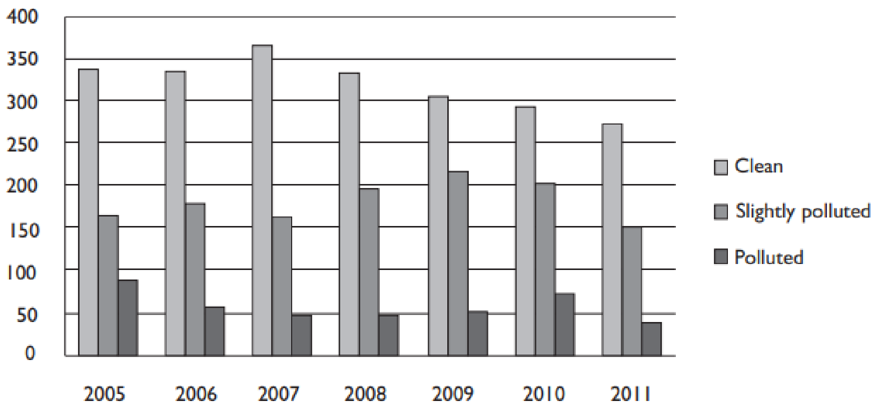

Figure 2.2: River Basins Water Quality Trend (2005–2011) in Malaysia

Source: Environmental Quality Report (EQR), 2011

2.3.1 Water Quality Index (WQI)

In order to make an assessment on river water quality, Malaysia's Department of Environment (DOE) uses the Water Quality Index (WQI). Under Malaysia's Interim National Water Quality Standard (INWQS), the WQI is the foundation for river evaluation in terms of classifying pollutant loads and identifying categories of beneficial uses. Water quality determination is critical because water is frequently used in daily life necessities. The purpose of water quality testing is to ensure that the water supply is safe to use. Water quality testing (the study of the physical, chemical, and biological characteristics of water) will provide information about the health of the waterways, such as whether they meet the requirements of biotic species to live or can be used by humans for a variety of purposes. Hence, the Water Quality Index (WQI) was created to track changes in water quality in a specific area by measuring six parameters, namely dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD), pH, ammonia nitrogen (AN), and total suspended solids (TSS) (Nurul-Ruhayu *et al.*, 2015).

There are five classes under WQI; Class I, Class IIA, Class IIB, Class III, Class IV, and Class V, whereby Class V is classified as extremely contaminated. The WQI approach is a physio-chemical-based assessment that excludes biological characteristics such as coliform and other forms of bacteria from determining the microbes present in the water. The WQI should incorporate factors such as focal uniform, heavy metals, oil, and grease. The river status reading is then accurate (Nurul-Ruhayu *et al.*, 2015). The WQI classification is shown in Table 2.2.

Parameter	Unit	Class				
		I	II	III	IV	V
Biochemical Oxygen Demand (BOD)	mg/L	<1	1-3	3-6	6-12	>12
Chemical Oxygen Demand (COD)	mg/L	<10	10-25	25-50	50-100	>100
Ammoniacal Nitrogen (AN)	mg/L	<0.1	0.1-0.3	0.3-0.9	0.9-2.7	>2.7
Dissolved Oxygen (DO)	mg/L	>7	5-7	3-5	1-3	<1
pH	mg/L	>7	6-7	5-6	<5	>5
Total Suspended Solid (TSS)	mg/L	<25	25-5-	50-150	150-300	>300
WQI	-	>92.7	76.5-92.7	51.9-76.5	31.0-51.9	<31.0

*WQI: 81-100 = Clean, 60-80 = slightly polluted and 0-59 = polluted

Table 2.2: Water Quality Index (WQI) for Malaysia

2.3.2 National Water Quality Standards (NWQS)

Malaysia's Department of Environment (DOE) initiated a comprehensive initiative to produce water quality standards and criteria in 1995. This study was carried out in five phases (I - IV). The beneficial applications were decided to prioritise residential water supply, fisheries and aquatic propagation, livestock drinking, recreational use, and agricultural use. In Phase I of the study, more than 120 physicochemical and biological properties for the proposed beneficial uses from regional and global literature are evaluated. The study's initial stage recommended a set of interim National Water Quality Standards (INQWS) that established six classes (I, IIA, IIB, III, IV, and V) to be used to classify rivers or river segments into quality classes in descending order. The National Water Quality Standards also include classification parameters such as heavy metals. Hence, the given standards can be also used to identify significant heavy metals present in water bodies such as rivers.

2.4 Causes of River Water Pollution

Water pollution can be caused by several factors, namely oil spills, discharge of industrial and household wastes, sewage release, intensive farming and use of pesticides in agriculture.

2.4.1 Point and Non-Point Sources of River Water Pollution

There are point and non-point sources of water pollution (Novotny and Chester, 1981). Point source pollution is usually a noticeable, confined pollution and relatively easy to estimate the pollution loads (Mamun and Salleh, 2014). Household sullage, sewage treatment plants, and industrial areas are identified as the main point sources. Apart from these, point sources include markets, restaurants, workshops, residential areas, solid waste disposal sites, soil and sand sourcing, new development areas, aquaculture, commercial lots, petrol stations, livestock, and others (Afroz *et al.*, 2014). Direct discharge of wastes from such sources results in the presence of heavy metals and other toxins in rivers, putting people and other organisms nearby in danger.

Non-point source pollution impacts a water body through dispersed sources, and it can come from a variety of places. Non-point source pollution is more difficult to control than point source pollution (Sanda *et al*, 2022). Non-point source pollution does not have a clearly defined entry point. The pollution may come from agriculture, street runoff, deposition of atmospheric pollutants, mine sites, transportation corridors such as roads and railways, etc. (Ongley, Xiaolan and Tao, 2010). On rainy days, the stormwater picks up heavy metals, soil, pesticides, herbicides, and other contaminants and transports them to rivers. As a result of the accumulation of these pollutants, the water quality deteriorates.

From the site investigation conducted at Perai River, it was found that there are numerous land use activities such as industrial, household and commercial (restaurants) activities along the shores of the river. Oil spills from fishermen's boats at the downstream of Perai River also add to the deterioration of river water quality.

2.4.2 Industrial and Municipal Activities

Industrial pollution happens due to the release of wastes generated from the industry into the rivers. Discharge from industries contains various organic and inorganic pollutants which may contain heavy metals. The toxicity and carcinogenicity of these heavy metals can cause harm to humans and other species. For instance, thousands of dead fishes were found floating in the Perai River during high tide on February 9, 2021, due to untreated detergents released by a food industry (Dermawan, 2021). Detergents contain many organic compounds and heavy metals such as Iron (Fe) and Manganese (Mn) (Barkodia *et al.*, 2020). Industries as such often release their pollutants into the atmosphere, water and soil. Therefore, this leads to the increase of metals in the river waters due to the activity of discharging untreated domestic and industrial wastes (Noorhosseini *et al.*, 2017).

Both heavy domestic activities and growing industries lead to tremendous chemical pollution. Many industrial and commercial undertakings contribute to regional economic development, but they can also become a severe threat to the deterioration of the environment’s quality. Heavy discharge from the domestic effluents into the river deteriorates the water quality and human health conditions (Venugopal *et al.*, 2009).

2.4.3 Solid Waste Disposal

The direct disposal of solid waste into rivers causes the river's quality to deteriorate. As a result, heavy metal-containing contaminants leach underground, contaminating aquifers that may be used for water supply and leaving them unfit for human use. Rapid industrial development and urbanisation have raised the quantity and diversity of toxic and 11 hazardous wastes (Abdullah, 1995). Urbanisation and industrialisation have changed the characteristics of solid waste generated (Manaf *et al.*, 2009).

Solid waste can comprise garbage, domestic refuse, and discarded solid materials from commercial, industrial, and agricultural productions (Ashraf *et al.*, 2014). Solid waste management is a severe challenge in the urban environment, particularly in quickly growing cities and towns in developing countries. As the amount of waste produced grows, the likelihood of solid waste pollution grows. In metropolitan places, solid waste management is becoming a major environmental and public health issue. When there is an excess of solid waste and proper management is not implemented, the wastes may end up in the river, affecting water quality.

2.5 Heavy Metals

A set of metals and metalloids with an atomic density larger than 4 g/cm3, or 5 times or greater than water, are referred to as heavy metals (Yahaya, Mohammad and Abdullahi, 2009). Heavy metals are also known as trace elements and even at very small concentrations, they can be highly toxic. A large number of heavy metal applications in industrial, domestic, agricultural, medical, and technological sectors have resulted in their widespread diffusion in the environment, raising worries about their possible health and environmental repercussions. Heavy metal toxicity is determined by several parameters, including the dose, route of exposure, and chemical species, as well as the age, gender, genetics, and nutritional state of those who have been exposed. Arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), and mercury (Hg) are among the priority metals of public health concern due to their high toxicity (Tchounwou *et al.*, 2012).

The term 'heavy metal' is widely documented and frequently applied to the widespread pollutants in soils and water bodies. Heavy metals' harmful character has been recognised due to their bioaccumulative propensity in biotic systems (Manmeet *et al.*, 2021). Speeding of urban development has increased the heavy metal contamination due to the intensified industrialisation and agriculture (Kamarudzaman *et al.*, 2018). As mentioned, direct disposal of industrial waste and spillage of oils are also some of the significant contributions to the existence of heavy metals in the water.

2.5.1 Effects of Heavy Metal Presence in River Water

The accumulation of heavy metals in water frequently leads to the degradation of water quality and an ecosystem catastrophe as a whole. Heavy metals are carried as dissolved species in water or as an integral element of suspended sediments across rivers and streams, whereby dissolved species in water have the highest potential for causing the most harmful effects (Duruibe *et al.*, 2007). Reactive oxygen species produced due to the existence of heavy metals and contaminants will incur damage to the aquatic organisms (Woo *et al.*, 2009).

Heavy metals have the ability to cause severe oxidative stress in aquatic creatures. Due to their high solubility in aquatic environments, heavy metals can be absorbed by living organisms, impacting the ecosystem's food chain (Ghazali and Marahel, 2021). The presence of contaminants in the food chain of the ecosystem may also affect the growth of animals and aquatic plants. This is because heavy metals such as As, Hg, Cd, Pb or Se are not ideal for optimal growth (Shukla, 2021). Large concentrations of heavy metals may also accumulate in the human body once the heavy metals reach the food chain (Sanjay *et al.*, 2021). Besides that, metals will not experience bacterial degradation, therefore, they will permanently remain in the river waters (Singh, 2011).

Long-term exposure to the pollutant will undeniably result in negative impacts on public health. This is because many heavy metal ions are known to be carcinogenic and are nonbiodegradable. Hence, it will accumulate in the tissues of living organisms, causing cancer (Mohan *et al.*, 2013). Other health effects caused by heavy metals include kidney diseases (lead, mercury and cadmium), joint diseases such as rheumatoid arthritis and neurological damage affecting IQ level (lead, arsenic) (Science Communication Unit, 2013).

2.5.2 ICP Analysis

ICP analysis, a potent chemical analysis technique, can be used to detect both minor concentrations and significant amounts of a variety of elements in a sample. Heavy metals are no exception in the list of elements that can be traced using this analysis. ICP Atomic Emission Spectroscopy (ICP-AES), often referred to as ICP Optical Emission Spectroscopy, and ICP Mass Spectrometry (ICP-MS) are some of the most common analysis methods conducted. ICP-MS provides a lower detection limit down to part per trillion (ppt), whereas ICP-OES offers both trace and significant concentrations over a wide variety of elements down to part per billion (ppb). Due to a number of positive characteristics, such as low detection limits, a broad linear dynamic range, and excellent precision, the inductively coupled plasma (ICP) has taken the lead as the primary source for quick spectroscopic multielement analysis (Olesik, 1991).

For practically all elements, intense emission is produced from a variety of spectral lines. The ICP is much more strongly excited when compared to flames or graphite furnaces. The ICP is so densely filled with excited states that strong emission is generated from numerous lines at once. A more rapid simultaneous analysis is therefore possible compared to a flame or graphite furnace which emits far less strong emissions. However, one of the main issues with ICP-OES is spectrum overlap, which is also due to the ICP's highly excited nature. The high temperatures could also mislead one into thinking that the sample has no impact on the plasma (Olesik, 1991).

The utilisation of liquid samples is necessary for ICP analysis. Therefore, for solid materials such as sediment samples, digestion is frequently needed. A plasma torch is used in ICP analysis to vaporise tiny droplets of the material. The atomic emission or ion mass is utilised to quantify the elements present in the sample, depending on the ICP analysis test method conducted.

2.6 Biochemical Oxygen Demand (BOD)

The biochemical oxygen demand (BOD) is an important environmental index for determining the relative oxygen requirements of wastewater, effluents, and polluted water (Kumar and Kumar, 2005). Biological oxygen demand (BOD) is the amount of dissolved oxygen required by aerobic biological organisms to break down organic material present in a particular water sample at a specific temperature and time period (Li and Liu, 2019). The BOD value is most usually stated in milligrams of oxygen used per litre of sample after a 5-day incubation period (BOD_5) at 20 °C and is frequently used as a surrogate for the degree of organic pollution in water (Virendra *et al.*, 2013). The BOD test, as used to assess wastewater treatment efficiency, is designed to measure a fraction of the carbonaceous oxygen demand, i.e., the oxygen consumed by heterotrophic microorganisms that use waste organic matter in their metabolism, rather than the oxygen demand exerted by autotrophic nitrifying bacteria. Because ammonia is commonly found in wastewater, nitrification inhibitors must be used to reduce nitrogenous oxygen demand. Carbonaceous oxygen demand is referred to as first-stage BOD, while nitrogenous oxygen demand is referred to as second-stage BOD (Kumar and Kumar, 2005).

The BOD_5 is helpful in three ways. First, it certifies that the wastewater discharge and waste treatment technique comply with current regulations. Second, the ratio of BOD5 to COD (chemical oxygen demand) in wastewater treatment plants represents the biodegradable fraction of an effluent. Third, the COD/BOD5 ratio indicates the size of a wastewater treatment plant needed at a specific location (Jouanneau *et al.*, 2014).

2.6.1 Causes and Effects of Excessive BOD in River Water

Organic pollution of rivers from municipal and industrial wastewater and diffuse runoff from agriculture severely impact aquatic ecosystems, including oxygen loss and changes in species composition. Severe organic pollution can rapidly de-oxygenate river water. Organic material discharged into natural waters also promotes the rapid growth of microbes, which deplete the essential oxygen for other aquatic life (Bajpai, 2018). The amount of dissolved oxygen in rivers and streams directly affects BOD (United States Environmental Protection Agency, 2012). As the amount of dissolved oxygen in rivers decreases, BOD increases.

High levels of organic pollution can cause high BOD, usually caused by poorly treated wastewater. High BOD can also be due to high nitrate levels, which trigger high plant growth. The higher the BOD, the faster oxygen is reduced in the stream. This means that higher types of aquatic life have less oxygen available to them. High BOD levels have the same consequences as low dissolved oxygen levels (United States Environmental Protection Agency, 2012). For instance, marine creatures may suffocate and die due to the lack of oxygen.

2.7 Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) is a measurement of the oxygen equivalent of organic matter in a water sample that is susceptible to oxidation by a strong chemical oxidant. COD is frequently used to gauge how susceptible organic and inorganic wastes, as well as municipal and industrial wastes, are to oxidation (Jain and Singh, 2003). COD is a water quality measure used to assess the amount of biologically active substances such as bacteria in water and the amount of biologically inactive organic matter. It is a significant and quick measure to characterise water bodies, sewage, industrial wastes, and treatment plant effluents (Khan and Ali, 2018). The COD test of natural water determines the total amount of oxygen necessary for the oxidation of waste to carbon dioxide and water (Jain and Singh, 2003).

2.7.1 Causes and Effects of Excessive COD in River Water

There are various causes of high COD in river water. Soluble organic compounds are one of the factors that lead to increased COD levels. COD concentrations in residual food waste from bottles and cans, and emulsified oils are all very high and are common contributors to COD in industrial wastewater. A high chemical oxygen demand in water suggests more elevated levels of oxidisable organic matter, resulting in a smaller amount of Dissolved Oxygen (DO). Organic contamination can cause critical DO depletion, which can be fatal to aquatic living. In addition, river water with high COD levels may have an unpleasant odour and appear murky or coloured, depending on the source of pollution.

2.8 Key Differences between BOD_5 and COD Tests

Only biologically reactive carbon is oxidised in a BOD test, whereas all organic matter is converted to carbon dioxide in a COD test. The COD test does not identify oxidisable material or distinguish between organic and inorganic material present. Likewise, it does not indicate the overall amount of organic carbon present. As a result, COD values are higher than BOD values (Jain and Singh, 2003). BOD test uses a population of bacteria and other microorganisms to replicate what would happen in a natural stream over five days. In contrast, the COD test uses a strong chemical oxidising agent (potassium dichromate or potassium permanganate) to chemically oxidise the organic material in the wastewater sample under heat and strong acid conditions (Woodard & Curran, Inc., 2006). The COD test has the advantage of not being affected by harmful compounds and taking only two or three hours to complete, as opposed to five days for the BOD test (Khan and Ali, 2018).

2.9 Statistical Package for Social Sciences (SPSS)

Statistical Package for Social Sciences (SPSS) is a statistical software suite developed by International Business Machines Corporation (IBM) for data management and statistical analysis of social science data. The software is commonly used by researchers for complex statistical data analysis such as multivariate analysis. Correlation is a statistical term that indicates the relationship between two variables. It describes how one variable responds when the other variable changes (Sereno, 2021). If two variables increase or decrease in parallel, they have a positive correlation; if one variable increase while the other decreases, they have a negative correlation. If changing one variable has no effect on another, the variables have a zero correlation.

If there is a relationship between variables in a dataset, the correlation coefficient value will indicate it. The detection of similarities between the variables is done using the correlation coefficient. The correlation coefficient's value ranges from -1 to 1, where -1 indicates a fully negative association, 0 indicates there is no relationship between the variables, and 1 indicates a perfectly positive relationship exists. The next step taken after determining the correlation between two variables is regression. The regression test determines how much one variable affects another (Beers, cited in Jain and Shetty, 2021). The results of the regression test are represented by a number of values. R square, Adjusted R square, F ratio, Beta value, Significance level, p-value, and T-statistic are the important terms for regression analysis values (Jain and Chetty, 2021).

CHAPTER 3

METHODOLOGY

3.1 Overview of Chapter

This chapter presents the physical experimental procedures of conducting the Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) test, biochemical oxygen demand (BOD) test and chemical oxygen demand (COD) test. ICP-OES test is done to identify the types of heavy metals present in Perai River water. The BOD test is conducted to determine how much oxygen microorganisms consume while decomposing organic matter in stream water, whereas the COD test is done to determine the amount of oxygen consumed by chemical reactions in water. The methodology covers the steps of conducting each test in detail, from the collection of samples to pollution contribution mapping using spatial distribution in GIS, and conducting a bivariate correlation analysis using SPSS software to identify the correlation between heavy metals distribution, COD and BOD. The problem statement can be attempted, and research objectives can be attained by following the research approach outlined in this study.

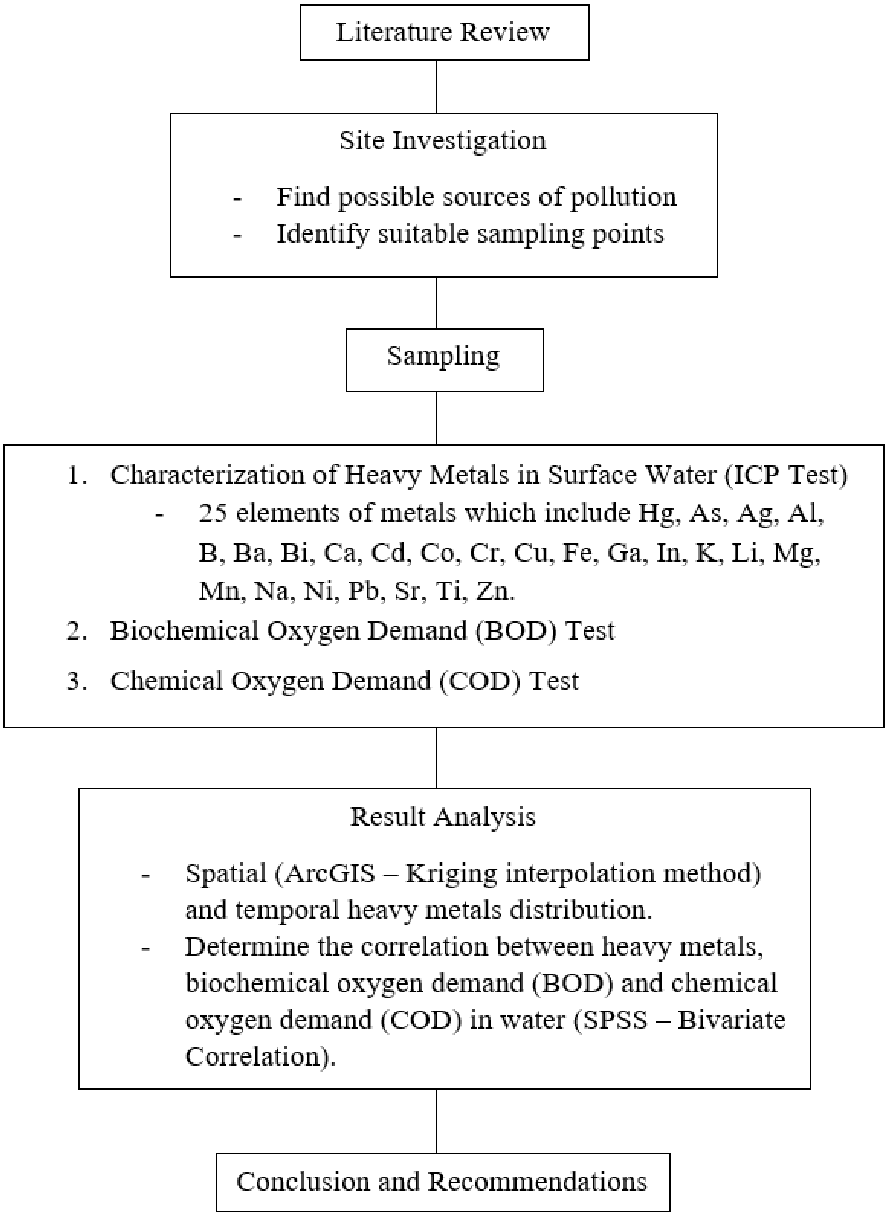

Figure 3.1: Flow Chart of Overall Study

3.2 Site Investigation

Site investigation is the process of collecting information and analysing any potential hazards or variables that may affect the research in the study area. The study area for this research is Perai River, Penang. Perai River is chosen for the research because of the large potential yield of raw water source, which is 136 million litres per day (Mok, 2020). During the site investigation, the possible sources of heavy metals